Chapter 3

Alkenes:

Structures, Nomenclature and an Introduction to Reactivity

Thermodynamics and Kinetics

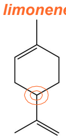
Adapted from Profs. Turro & Breslow, Columbia University and Prof. Irene Lee, Case Western Reserve University

Ever put an apple into a bag with green tomatoes or a green banana?

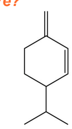
Natural Products: $CH_2{=}CH_2$

muscalure
sex attractant of the house fly

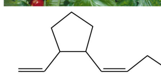
What might account for the difference between lemon and orange in the limonene structure?



limonene
from lemon and orange oils



β-phellandrene
oil of eucalyptus



multifidene
sex attractant of brown algae

Molecular Formulas of Alkenes

Saturated vs. Unsaturated: *Missing Hydrogens*

$CH_3CH_2CH_2CH_3$
a saturated hydrocarbon

$CH_3CH{=}CHCH_3$
an unsaturated hydrocarbon

Alkanes are completely "saturated"
i.e. only single bonds

Each double bond has 1 degree of unsaturation.
Each ring has 1 degree of unsaturation.
Each triple bond is 2 degrees of unsaturation.

Compare a molecular formula to an alkane's: every TWO *Hydrogens less = I degree of unsaturation*

Molecular Formulas of Alkenes

Saturated vs. Unsaturated: *Missing Hydrogens*

Noncyclic alkene:
C_nH_{2n}
1 degree of unsaturation

Cyclic alkene:
C_nH_{2n-2}
(Same as an alkyne;
2 degrees of unsaturation)

$CH_3CH_2CH_2CH_2CH_3$
an alkane
C_5H_{12}
C_nH_{2n+2}

$CH_3CH_2CH_2CH{=}CH_2$
an alkene
C_5H_{10}
C_nH_{2n}

a cyclic alkane
C_5H_{10}
C_nH_{2n}

a cyclic alkene
C_5H_8
C_nH_{2n-2}

Systematic Nomenclature of Alkenes

•Follows alkane rules; treats double bond as a function: Think of alcohols

$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2$
1-butene

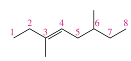
$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_3$
2-butene

$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$
2-hexene

$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}(={}^{1}CH_2)CH_2CH_2CH_3$
2-propyl-1-hexene

the longest continuous chain has eight carbons but the longest continuous chain containing the functional group has six carbons, so the parent name of the compound is hexene

•Substituents in alphabetical order with lowest numbers

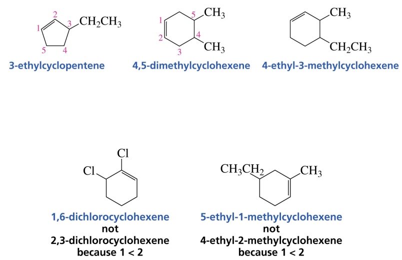


$\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H(Br)\overset{4}{C}H(Cl)\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2$

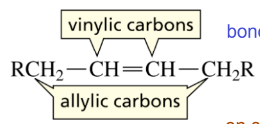
$CH_3CH_2CH_2C(CH_3){=}CHCH_2CH(CH_3)CH_3$
2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because 2 < 4

$CH_3CH(Br)CH{=}C(CH_3)CH_2CH_3$
2-bromo-4-methyl-3-hexene
not
5-bromo-3-methyl-3-hexene
because 2 < 3

•Cyclic alkenes:



Important Special Terms

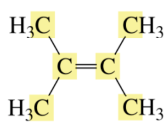


Vinyl Hs:
bonded to the double bond.

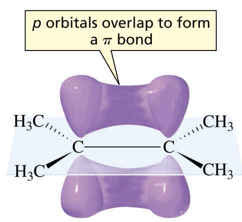
Allylic Hs:
on sp3 carbons next to the double bond.

	$H_2C{=}CH{-}$ the vinyl group	$H_2C{=}CHCH_2{-}$ the allyl group
	$H_2C{=}CHCl$	$H_2C{=}CHCH_2Br$
systematic name:	chloroethene	3-bromopropene
common name:	vinyl chloride	allyl bromide

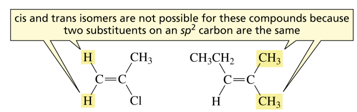
Structure of Alkenes

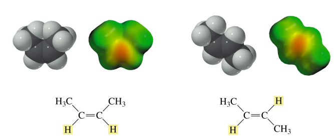


the six carbon atoms are in the same plane

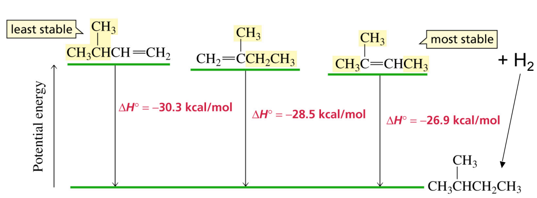


Isomers of Alkene





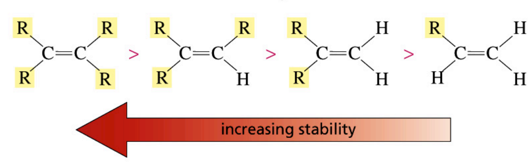
Relative Stabilities of Pentene Isomers



Relative Stabilities of Alkenes

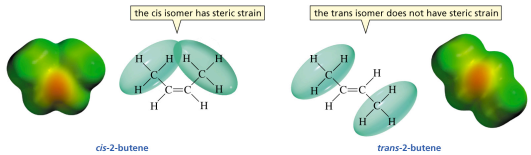
Δ H $_{hydrogenation}$ C_4H_8 = -117.8+/-0.42; - 125.9 kJ / mol

relative stabilities of alkyl-substituted alkenes

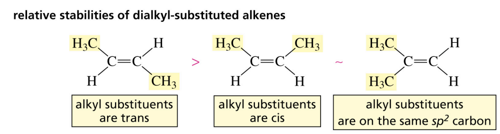


Where do cis- and trans- fit?
ΔH $_{hydrogenation}$ cis 2-butene= - 118.5 +/- 0.42 kJ / mol
Δ H $_{hydrogenation}$ trans 2-butene= - 114.6 kJ / mol

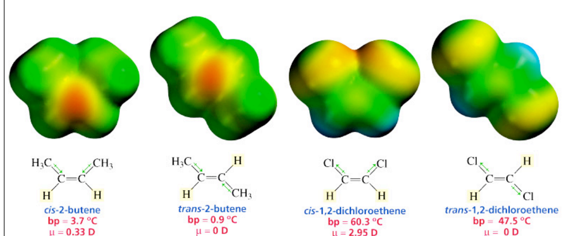
Steric Strain in Alkenes



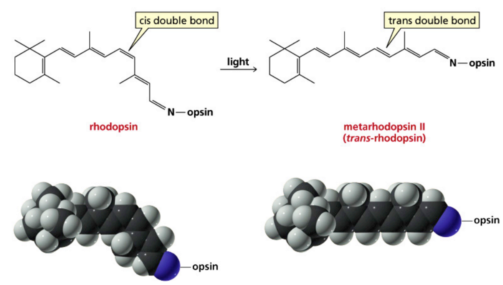
Relative Stabilities of Dialkyl-Substituted Alkenes



Dipole Moments of Alkene Isomers



Cis-Trans Isomerization & Vision



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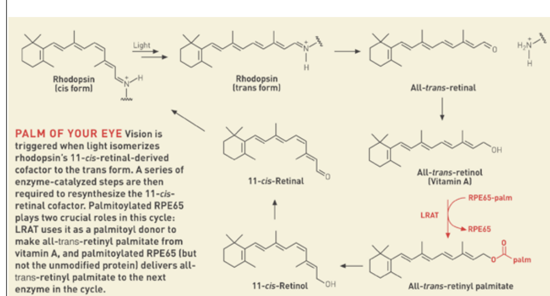

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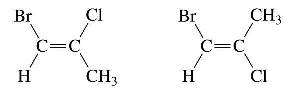


Which isomer is cis and which is trans?

E and Z isomers

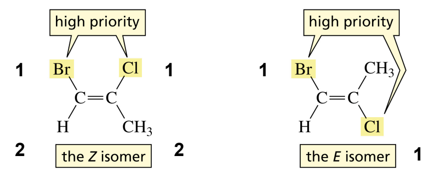
Priority is in order of atomic number.
Rank H vs. Br and C vs. Cl.

Naming using E, Z

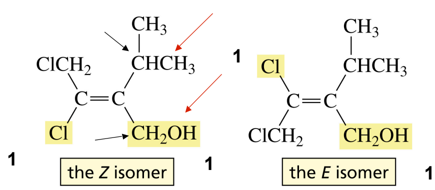
E (entgegen:opposite): Z (zusammen; same)

Consider the atomic number of the atoms bonded directly to a specific sp^2 carbon

1,1 on same side = Z ***1,1 on opposite sides = E***

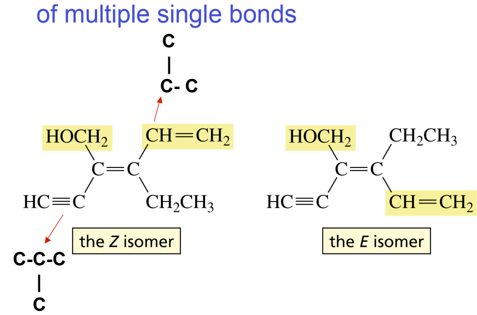


If the atoms are the same, eg. the carbon atoms: then consider the other atoms that are attached to them.

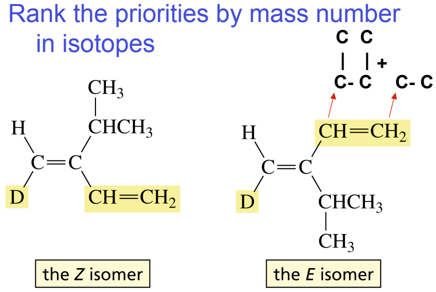


O vs C

Multiple bonds are treated as attachments of multiple single bonds



Rank the priorities by mass number in isotopes

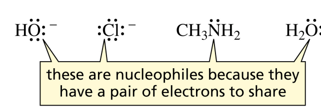


An alkene is an electron rich molecule, a nucleophile.

"nucleophile"- likes nuclei (likes protons: H+)

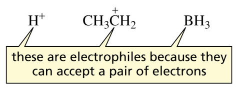
Nucleophiles: electron-rich atoms or molecules that react with electrophiles.

"electrophile"- likes electrons (likes minus: e- and anions) Examples of nucleophiles



Nucleophiles are attracted to electron-deficient atoms or molecules (electrophiles)

Examples of Electrophiles



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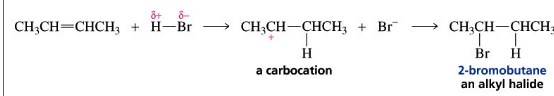
Electrophilic Addition of HBr to Alkene

A two step reaction.
Mechanistic path of a reaction:
how reactants form products.



How can a mechanism be illustrated?
i.e. bond making & bond breaking

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Using Curved Arrows in Reaction Mechanisms

Movement of a pair of electrons:

START arrows from electrons pointing to electrophile

Use 1/2 arrow for the movement of one electron

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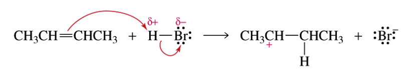
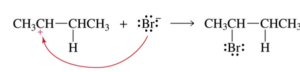
Using Curved Arrows





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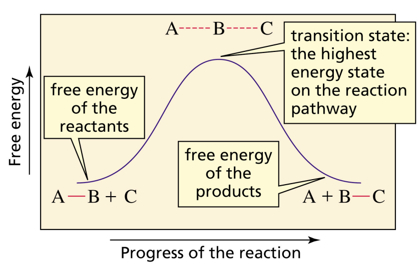
Reaction Coordinate or Energy Diagram



Transition states have partially formed bonds

Intermediates have fully formed bonds

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Thermodynamic Parameters

$\Delta G^o = \Delta H^o - T\Delta S^o$

Gibbs standard free energy change (ΔG^o)

Enthalphy (ΔH^o): the heat given off or absorbed during a reaction

Entropy (ΔS^o): a measure of freedom of motion

If ΔS^o is small compared to ΔH^o, $\Delta G^o \sim \Delta H^o$

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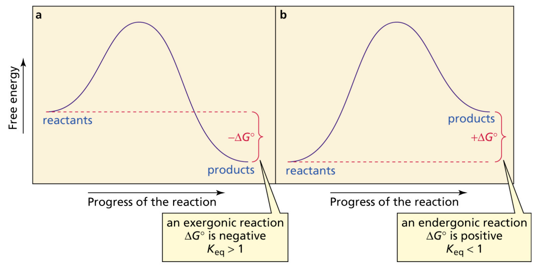
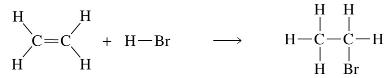


Exergonic Reaction
-ΔGo

Endergonic Reaction
+ΔGo

ΔH o for any reaction can be calculated from bond dissociation energies



bonds being broken		bonds being formed	
π bond of ethene	$\Delta H° =$ 63 kcal/mol	C—H	$\Delta H° =$ 101 kcal/mol
H—Br	$\Delta H° =$ 87 kcal/mol	C—Br	$\Delta H° =$ 69 kcal/mol
	$\Delta H°_{total} =$ 150 kcal/mol		$\Delta H°_{total} =$ 170 kcal/mol

$\Delta H°$ for the reaction $= \Delta H°$ for bonds being broken $- \Delta H°$ for bonds being formed

$= 150$ kcal/mol $- 170$ kcal/mol

$= -20$ kcal/mol

Kinetics deals with the rate of chemical reactions and the reaction mechanism

Rate of a reaction =

(number of collision per unit time) x (fraction with sufficient energy) x (fraction with proper orientation)

$$\mathbf{A} \longrightarrow \mathbf{B}$$

rate ∝ [A]

$$\mathbf{A} + \mathbf{B} \longrightarrow \mathbf{C} + \mathbf{D}$$

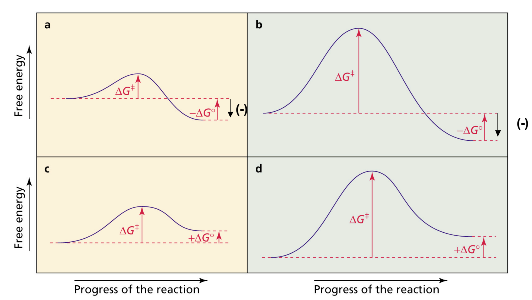
rate = k[A][B]

$$\mathbf{A} + \mathbf{A} \longrightarrow \mathbf{B}$$

rate = $k[A]^2$

The rate-limiting step controls the overall rates of the reaction

The free energy of activation & the transition state and the reactants



$\Delta G^‡ = \Delta H^‡ - T\Delta S^‡$

$\Delta G^‡$:
(free energy of transition state)- (free energy of reactants)

$\Delta H^‡$:
(enthalpy of transition state) - (enthalpy of reactants)

$\Delta S^‡$:
(entropy of transition state) - (entropy of reactants)

Rates and Rate Constants

First-order reaction

A ⟶ B

rate = *k* [A]

Second-order reaction

A + B ⟶ C + D

rate = *k* [A][B]

The Arrhenius Equation

$k = Ae^{-E_a/RT}$ $\qquad$ $E_a = \Delta H^{\ddagger} + RT$

Rate Constants and the Equilibrium Constant

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$K_{eq} = k_1/k_{-1} = [B]/[A]$

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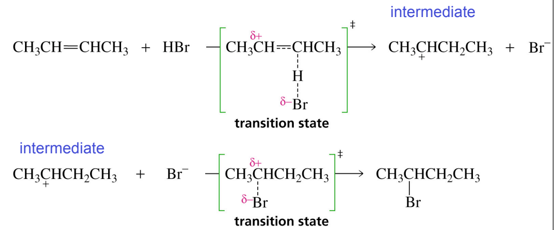
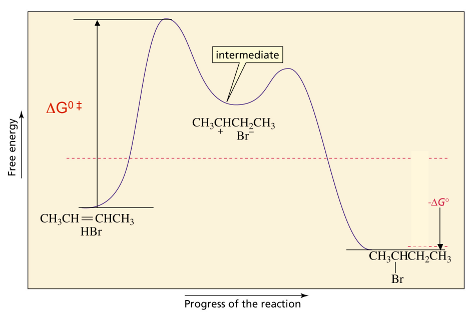
Transition State Versus Intermediate



Transition states have partially formed bonds

Intermediates have fully formed bonds

Electrophilic Addition of HBr to 2-Butene



The rate-limiting step controls the overall rates of the Reaction. It has the highest activation energy.

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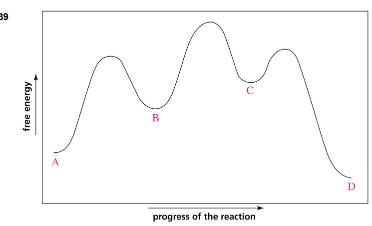
Problem 3.39



a. How many intermediates are there in the reaction?
b. How many transition states are there?
c. What is the fastest step in the reaction?
d. Which is more stable, A or D?
e. What is the reactant of the rate-determining step?
f. Is the first step of the reaction exergonic or endergonic?
g. Is the overall reaction exergonic or endergonic?

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10a
Addition of Hydrogen Halides to Alkenes 1

Why does the proton add to one carbon preferably over the other?
(The reaction is *regioselective*.)

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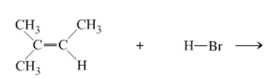
Drag the π bond to the more electrophilic atom of HBr.



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